Microstructure and Carburization Detection in HP Alloy Pyrolysis Tubes

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Abstract A highly carburized HP40-Mod alloy ethylene pyrolysis tube was characterized by means of scanning electron microscopy with backscatter electron imaging, electron back-scattered diffraction, energy dispersive spectroscopy, and etching using the NACE International Standard Test Method for evaluation of carburization of ethylene pyrolysis tubes. The response of the tube to eddy current non-destructive testing was measured using the carburization crawler under development at Quest Integrity NZL Ltd. The matrix was significantly depleted of chromium, as low as 4 wt% Cr at the inner wall. $M_{23}C_6$ carbides transformed to M_7C_3 at the inner wall region and NbC carbides partially transformed to the chromium-rich η -carbide at the outer wall region, both of which likely contributed to the chromium depletion of the matrix. The present results indicate that the NACE etchant attacks the austenitic matrix where chromium content is below approximately 12wt%. A comparison to other ex-service tubes indicates that matrix chromium content and the location of the $M_{23}C_6/M_7C_3$ transformation front are useful microstructural characteristics for interpreting eddy current NDT response.

Keywords Scanning Electron Microscopy · Steels · Phase transformations · Metallography

Introduction

Ethylene is used extensively in the production of plastics, cabling, and automotive products, and is typically produced by the thermal cracking (pyrolysis) of more complex hydrocarbons, such as naphtha or ethane, at 700–1100 °C inside a tube in a pyrolysis furnace. In order to provide the corrosion resistance and creep strength necessary to withstand such harsh operating conditions, the heat resisting (H-series) centrifugally cast, austenitic stainless steels are typically used for pyrolysis tubes [1, 2].

Carburization is one of the major degradation mechanisms of pyrolysis tubes [3]. High carbon potentials at the inner diameter due to the cracking reaction and high tube temperatures result in the diffusion of carbon into the tubes, where it combines with chromium and other carbide-forming elements to grow existing carbides and create new ones [4, 5]. The carbides undergo chemical and morphological changes, initially coarsening and coalescing, followed by phase transformation [4].

Internal carbide precipitation results in considerable volume increases, changes in thermal expansion coefficient of the carburized zone, and embrittlement. The result is a reduction in ductility as well as increase in internal stresses, adversely affecting the creep properties and the ability of the tube to withstand thermal cycling [2, 5–8].

Consequently, there is interest in non-destructive testing (NDT) methods to evaluate the level of carburization of tubes in situ. Carbide precipitation and the segregation of elements in HP alloy tubes result in a change in the magnetic properties of the carburized region, allowing

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carburization to be detected non-destructively using eddy current techniques [6, 7, 9]. However, the eddy current systems require calibration using ex-service pyrolysis tubes that have had their microstructure, mechanical properties, and magnetic response characterized [6, 9].

This paper presents the results of detailed microstructural characterization of a highly carburized ex-service ethylene pyrolysis tube. The purpose of the paper is to determine whether there are certain microstructural features or compositional variations (e.g., chromium depletion) that dictate the eddy current NDT response of ex-service tubes.

Materials and Methods

An ex-service HP40-Mod alloy ethylene pyrolysis tube was examined. It had spent approximately 4 years in service, at 20 psig and 1300 °F (138 kPag and 704 °C). The typical as-cast composition of an HP40-Mod alloy is given in Table 1 [10]. The tube had an outer diameter of 100 mm, and an average wall thickness of 7.7 mm.

A ring approximately 10-mm thick was cut from the tube, and a metallographic sample approximately 8×10 mm was sectioned and mounted in order to observe the through-wall face. The sample was ground on SiC paper at 180, 240, 320, 400, and 600 grit, then polished with 9 and 3 μm diamond suspension. A final polish to a 0.02- μm finish was achieved using colloidal silica. Prior to electron back-scattered diffraction (EBSD) analysis, the sample was etched in glyceresia for 10 s, in order to increase the visibility of the precipitates. The composition of the glyceresia was 30 ml of glycerol, 30 ml of hydrochloric acid, and 10 ml of nitric acid.

Phase identification was carried out using a JEOL JSM 7000 field emission scanning electron microscope (FE-SEM), equipped with a JEOL JED-2300 energy dispersive x-ray spectroscopy (EDS) system, and a JEOL 6100 SEM, equipped with an Oxford HKL Channel 5 EBSD system. A combination of back scatter electron (BSE) imaging, EDS, and EBSD was used to identify the precipitate phases present in the tubes and determine their locations across the tube wall. BSE images were taken at set intervals across the tube wall, with multiple EDS spectra taken for each phase at each location. The appearance of each phase in the BSE images and the composition determined by EDS were used to produce a list of candidates for each phase. Crystal structure was then confirmed using EBSD.

The chromium depletion of the matrix was measured using EDS. The spectra were taken at a distance of

approximately 10 μm from primary chromium carbides. In the highly carburized region of the sample, 10 μm was approximately the distance at which a point in the matrix was equidistant from surrounding chromium carbides.

Progressive deep etching was used in order to gain an understanding of the three-dimensional structure of the carbide network. The sample was imaged in BSE mode at multiple locations in the as-polished condition, and the same locations were imaged in SEI mode after 15, 30, 60, 120, and 180 min etching using glyceresia. Glyceresia was chosen as the etchant as in HP alloys it only etches away austenite, leaving the carbide network intact [10].

The etching method described in the NACE International Standard Test Method for evaluation of carburization of ethylene pyrolysis tubes [11] was used to semi-quantitatively measure the extent of carburization in the ex-service tube. The etchant was composed of 200 ml of nitric acid, 70 ml of hydrofluoric acid, and 670 ml of distilled water. The etching sample was taken from the sectioned ring, adjacent to the metallographic sample. Upon completion of the etching, the sample was observed under an Olympus SZH10 stereo-optical microscope.

Precipitate—matrix orientation relationships were analyzed using EBSD. EBSD patterns (EBSPs) were obtained from the precipitates and the austenitic matrix directly adjacent to each precipitate. The Euler angles (ϕ_1 , ϕ_2 , Φ) that describe the crystallographic orientation with respect to a reference axis system were calculated from the indexed EBSPs. The Euler angles were used to calculate an orientation matrix for each point of analysis, and then the misorientation between the two points was calculated. The disorientation (i.e., the variant with the smallest rotation angle θ about the rotation axis $[u \ v \ w]$) was then calculated by considering symmetry operations, e.g., the 24 crystallographic equivalents for the cubic system [12].

The eddy current NDT response of the ex-service tube was measured using the eddy current NDT carburization crawler that is being developed by Quest Integrity NZL Ltd. The system uses cylindrical coils to probe the tube with variable frequency electromagnetic waves, and measures the changes in coil properties (i.e., inductance, resistance), which differ depending on the level of carburization of the tube.

Results and Discussion

Macrostructure

Figure 1 shows the through-wall grain structure of the tube. Centrifugally cast HP alloy tubes display either a completely columnar structure or a mixed columnar-equiaxed structure, depending on the centrifugal casting conditions

Table 1 Typical Composition of an HP40-Mod alloy [10]

Wt%	C	Cr	Ni	Nb	Si	Mn	Fe
HP-40-Mod	0.4	25	35	1.5	1.5	1.5	Bal.

Fig. 1 Low-magnification image showing the through-wall grain structure of the ex-service tube (etchant: Marbles reagent)

(for example, the pouring temperature and the cooling rate) [13–15]. The 100% columnar structure of the ex-service tube indicates a high cooling rate induced during casting.

Phase Identification

A number of different phases were present across the wall thickness of the ex-service tube, including carbides, carbonitrides, and silicon-rich phases. A schematic of the tube wall summarizing the locations of interest and the phases identified is shown in Fig. 2.

Chromium Carbides

The microstructure across the tube wall consisted of an austenitic matrix with a network of coarse chromium-rich carbides and niobium-rich carbides. The chromium-rich carbides in the 0.4–5 mm region of the tube wall were identified as M_7C_3 (where $M = Fe, Cr, Ni$), and those in the 5–7.2 mm region were identified as $M_{23}C_6$. The niobium-rich carbides were identified as NbC.

The progression of the microstructure in the 0.4–5 mm region of the tube wall is shown in Fig. 3. The ratio of Cr to Fe in the M_7C_3 carbides increased as the distance into the tube wall from the inner diameter increased, as shown in Fig. 4. The Ni content remained constant at 1–2 at.%.

M_7C_3 is formed by the conversion of $M_{23}C_6$, as a result of the increasing C/Cr ratio at the inner wall region due to carbon diffusion from the inner diameter [5]. The composition of the M_7C_3 depends on the local carbon activity [16, 17], and thus, in the ex-service tube, on the distance from the inner diameter. The main metal component of M_7C_3 is Cr, but with increasing carbon activity an increased amount of iron is substituted for chromium [17–19].

The $M_7C_3/M_{23}C_6$ transformation front was located at a distance of approximately 5 mm from the inner diameter of the tube. The $M_{23}C_6$ carbide had a medium gray contrast in the BSE images, as shown in Fig. 5. The transition between

Fig. 2 Schematic of the tube wall summarizing the locations of the phases identified

M_7C_3 and $M_{23}C_6$ occurred over a very narrow range, with a band of approximately 200 μm in width where both M_7C_3 and $M_{23}C_6$ were present.

The appearance of the M_7C_3 carbides changed across the wall, with a separate phase appearing to be encapsulated, or contained, within the M_7C_3 , giving a “porous” appearance in two dimensions. The contained phase was present in the carbides across the 0.4–5 mm wall region, but appeared to become more prevalent as distance from the inner diameter increased, as evidenced in Fig. 3. The M_7C_3 carbides at a distance of 5 mm into the tube wall appear significantly more “porous” than those closer to the inner diameter. EDS and EBSD analysis identified the contained phase as austenite.

The “porous” appearance of the M_7C_3 carbides, without identifying the phase present inside the carbides, was previously reported by Christ [17] to occur during carburization of a 304L type stainless steel, and by Waldenström [20] in a Fe–Cr–Ni–Mn–C alloy. Kaya [4] also observed this phenomenon in an ex-service HK40 alloy ethylene pyrolysis tube, identifying the phase present inside the M_7C_3 carbides as austenite. All three studies attribute the “porous” appearance of the M_7C_3 carbides to its transformation from $M_{23}C_6$ by a eutectoid reaction during carburization, with Kaya defining the transformation as $M_{23}C_6 \rightarrow M_7C_3 + \gamma$ (where γ = austenite).

Kaya proposed that the excess elements (presumably Fe, Cr, and Ni [18], as M_7C_3 has a lower ratio of M to C) that cannot be accommodated in the M_7C_3 carbides upon the transformation from $M_{23}C_6$ would form the austenite phase regions in the M_7C_3 carbides, and that these austenite regions may nucleate on the $M_{23}C_6/M_7C_3$ transformation

Fig. 3 BSE micrographs of the microstructure at (a) 1.0 mm, (b) 3.0 mm, and (c) 5.0 mm from the inner diameter

Fig. 4 Change in composition of the M_7C_3 carbides with distance from the inner diameter. Results from three EDS spectra were averaged at each location

Fig. 5 BSE micrograph indicating the phases present at the M_7C_3 / $M_{23}C_6$ transformation front

front, or alternatively behind the moving front on the defects present in the M_7C_3 carbides.

EBSD analysis of 65 contained austenite–matrix pairs enabled the disorientation between the contained austenite regions and the adjacent austenitic matrix to be calculated. Figure 6 shows the relative frequency of the disorientation angle. 69% of the analyzed contained austenite pairs had a disorientation of less than 10° , typical of a cube–cube orientation with the austenitic matrix. 18% of the analyzed pairs displayed disorientations close to 60° , and the calculated disorientation axes for these pairs were close to $[111]$ —typical of a twin orientation. The remaining contained austenite displayed no particular orientation

Fig. 6 Relative frequency of angle of disorientation for contained austenite—austenitic matrix pairs

relationship with the austenitic matrix, indicating that no other rational orientations were obtained.

Progressive deep etching (Fig. 7) revealed that areas that appeared as open matrix in the as-polished condition became enclosed by M_7C_3 carbides beneath the plane of polish. If the plane of polish was further down into the sample, these regions would have appeared as austenite contained within the M_7C_3 carbides. Even though the carbide network may have appeared disconnected in the as-polished condition, the deep etch revealed that the carbides have a high level of connectivity in three dimensions.

Near the inner diameter of the tube, the M_7C_3 carbides appeared to be composed of many rounded grains which were very closely packed. Closer to the $M_7C_3/M_{23}C_6$ transformation front, there were regions where the M_7C_3 grains were closely packed, but also regions where the grains were more loosely packed, as shown in Fig. 8. If the plane of polish had been further down in the sample, the gaps in between the grains in the loosely packed regions would have appeared as austenite contained by M_7C_3 carbides in two dimensions. In contrast to the M_7C_3 carbides, the $M_{23}C_6$ carbides appeared to be composed of many closely packed angular grains, as shown in Fig. 9.

The space groups and lattice parameters of the M_7C_3 and $M_{23}C_6$ carbides, and of austenite, are summarized in Table 2 [15, 21]. In the as-cast condition, M_7C_3 does not have an orientation relationship with the austenitic matrix [19]. The $M_{23}C_6$ carbides are typically observed to have a cube–cube orientation relationship with the matrix [19, 22], the same crystal structure and a lattice parameter almost exactly three times that of the matrix. No orientation relationship between the M_7C_3 carbides that transform

from $M_{23}C_6$ as a result of carburization and the matrix has been reported.

Based on the orientation results and information in literature, there are a number of possible options for the formation of the austenite regions that appear contained by the M_7C_3 carbides:

- If the austenite regions are individual precipitates separate from the matrix:
 - If M_7C_3 in the carburized condition has no rational OR with the austenitic matrix, then the austenite regions must have nucleated in $M_{23}C_6$ or at the transformation front. A schematic portraying how this may occur at the transformation front is seen in Fig. 10(a).
 - If M_7C_3 in the carburized condition does have a rational OR with the matrix, the austenite regions may gain an OR by having M_7C_3 present at the point of nucleation. Nucleation could occur at or behind the transformation front.
 - The decomposition of $M_{23}C_6$ may begin at the $M_{23}C_6$ /austenite interface with growth of existing austenite cooperatively with M_7C_3 . In this case, the austenitic regions that appear contained by the M_7C_3 carbides would be expected to be connected to the matrix in three dimensions. It is possible that the twin growth direction may be more favorable than the normal growth direction in some cases. A schematic of how the austenite matrix may grow cooperatively with M_7C_3 is shown in Fig. 10(b).
- From the deep etching results, it seems more likely that the austenite regions that appear contained by the M_7C_3 carbides are connected to the matrix in three dimensions, as opposed to being individual precipitates separate from the matrix. The gaps in between the M_7C_3 carbide grains after deep etching appear more prevalent closer to the transition than at near the inner diameter, as do the austenite regions that appear contained by the carbides in the as-polished condition. It is possible that the contained austenite regions are the gaps in between the grains, and appear contained by the M_7C_3 carbides due to sectioning effects.

Cr–Ni–Nb–Si Rich Phase

In the 3.5–7.2 mm region of the wall, a phase rich in silicon, nickel, niobium, and chromium was observed, with a light gray contrast in BSE images in comparison to the darker gray chromium carbides. The average composition measured by EDS is shown in Fig. 11. The Cr–Ni–Nb–Si rich phase appeared to be transformed from NbC, and the area covered by this phase appeared to increase as distance from the inner diameter increased.

Fig. 7 M_7C_3 carbides (a) and (b) 1.0 mm from the inner diameter, as polished (BSE) and after 30 min in glyceresia (SEI) respectively. (c) and (d) 3.0 mm from the inner diameter, as polished (BSE) and after 120 min in glyceresia (SEI) respectively

The instability of NbC precipitates at temperatures of 700–1050 °C has been well reported in the literature [1, 22–27]. The product of the transformation is generally identified as G-phase, which has a commonly reported composition of $Ni_{16}Nb_6Si_7$, and an FCC structure with a lattice parameter of 1.12 nm [1, 23, 24].

The transformed phase identified in the ex-service tube contained Nb, Ni, and Si. However, it also contained a significant amount of chromium (determined by EDS as 42.5 at.%), and the Ni content was significantly lower (32.5 at.%), than the values typically reported for G-phase (approximately 55 at.%).

Another phase, the diamond cubic η -carbide, has also been identified in ex-service HP–Nb reformer tubes and aged HP–Nb alloy [10, 22, 25–27]. The typical composition of the transformed phase in the ex-service pyrolysis tube closely resembled the reported compositions. Despite

ambiguity in the EBSD analysis due to the similar space groups and lattice parameters of G-phase and η -carbide, the comparison between the composition of the transformed phase (Fig. 11) to reported values was considered sufficient evidence to identify the transformed phase in the ex-service tube as η -carbide, as opposed to G-phase. As η -carbide contains a significant amount of chromium, it is likely that the NbC-to- η -carbide transformation contributes to the chromium depletion of the matrix.

The current literature on the NbC-to-G-phase and NbC-to- η -carbide transformations in HP–Nb alloys is constrained to ex-service reformer tubes [8, 22, 25–27] and a limited number of laboratory-aged studies [1, 23–25]. Based on the available literature and data from laboratory-aged HP–Nb alloys, Buchanan [10] concluded that the NbC-to-G-phase and NbC-to- η -carbide transformations in aged HP–Nb alloys are dictated by the aging temperature.

Fig. 8 SEI images of M_7C_3 carbides at (a) inner diameter region and (b) inner diameter side of the $M_7C_3/M_{23}C_6$ transition after 180 min in glycerine

At temperatures below 875 °C the NbC-to-G-phase transformation dominates. Between 875 and 920 °C, the NbC-to-G-phase and NbC-to- η -carbide transformations can occur in parallel, and the η -carbide volume fraction is expected to increase with aging temperature until the NbC-to- η -carbide transformation becomes dominant, up to an upper limit of 1050 °C above which NbC carbides are stable.

As a result of carburization during service, the pyrolysis tube has a continual composition gradient across the tube wall (both for the austenitic matrix and the M_7C_3 carbides), and has a phase transformation front where $M_{23}C_6$ transforms to M_7C_3 , along with microstructural changes (such as the instability of NbC) associated with long term aging. There is also significant coarsening of the carbides in

Fig. 9 SEI image of $M_{23}C_6$ carbides on the outer diameter side of the $M_7C_3/M_{23}C_6$ transition, after 180 min in glycerine

highly carburized areas of the tube wall. The combination of these factors creates significantly different conditions within the pyrolysis tube compared to ex-service reformer tubes and laboratory-aged alloys. It is highly likely that the difference in conditions results in the temperature ranges over which the NbC-to-G-phase and NbC-to- η -carbide transformation occur in pyrolysis tubes to differ from those seen in the ex-service reformer tubes and laboratory aged alloys. This is evidenced by the ex-service pyrolysis tube's service temperature of 704 °C, along with the presence of η -carbide and lack of G-phase in the microstructure.

Inner and Outer Oxide Scales, Carbonitrides

At the inner diameter of the tube, a chromium-rich oxide scale with a depth of 100 μm was present. Inwards of the chromium oxide scale, a band of dendritic silicon oxides 250–300- μm thick penetrated into the tube (Fig. 12). Within this band, no chromium-rich precipitates were found, with only NbC carbides identified.

An oxide scale was also present at the outer diameter, with a layer composed of chromium oxides and silicon oxides 100–150- μm thick. The silicon oxides penetrated into the tube across a band 200–300- μm thick. This band was also free of chromium-rich precipitates (Fig. 13) with only NbC carbides present.

The presence of a chromium-rich oxide scale results in the depletion of chromium in the matrix adjacent to the scale, leading to a Cr-depleted zone free of chromium-rich precipitates. The Cr- and Si-rich oxide scales and the chromium precipitate free zone that were observed at the inner and outer diameters of the ex-service tube are consistent with observations of HP alloys exposed to oxidizing and carburizing environments at elevated temperatures [28, 29].

Table 2 Space groups and lattice parameters of relevant chromium carbides and the austenitic matrix [15, 21]

Phase	Space group	Lattice parameter
M_7C_3	Pnma	$a = 0.453 \text{ nm}$, $b = 0.701 \text{ nm}$, $c = 1.21 \text{ nm}$
$M_{23}C_6$	Fm $\bar{3}m$	$a = 1.066 \text{ nm}$
Austenite	Fm $\bar{3}m$	$a = 0.366 \text{ nm}$

Fig. 10 (a) Schematic of how austenite may precipitate as individual precipitates at the $M_7C_3/M_{23}C_6$ transformation front, (b) schematic of how the austenite matrix may grow cooperatively with M_7C_3 at the $M_7C_3/M_{23}C_6$ transformation front

Inwards from the chromium-rich precipitate free zone at the outer diameter, the $M_{23}C_6$ carbides in the carbide network transformed into a different chromium-rich precipitate, which had a blocky appearance and a darker contrast in BSE images compared to the medium gray $M_{23}C_6$ carbides. Lath-shaped precipitates of the same contrast were observed to have precipitated intragranularly. Both the lath-shaped precipitates and the blocky precipitates transformed from $M_{23}C_6$ were identified as $Cr_2(C,N)$, a carbonitride. It appeared that the majority of the $M_{23}C_6$ within a narrow band of $<200 \mu\text{m}$ had transformed into $Cr_2(C,N)$, with some of the $M_{23}C_6$ carbides further into the tube having also transformed into $Cr_2(C,N)$ (Fig. 13). The transformation of $M_{23}C_6$ to $Cr_2(C,N)$ and the precipitation of $Cr_2(C,N)$ at the outer diameter of the tube occurs due to the exposure of the tube's outer surface to the flue gases present in the furnace during service. Nitrogen diffusion into the tube results in the precipitation of $Cr_2(C,N)$ and the conversion of $M_{23}C_6$ to $Cr_2(C,N)$, which can then continue to grow by uptake of chromium and nitrogen [3]. The

Fig. 11 (a) typical composition of the Cr-Ni-Nb-Si rich phase as determined by EDS, (b) BSE micrograph showing the transformation of NbC to a Cr-Ni-Nb-Si rich phase

changes in materials properties due to nitriding are very similar to those due to carburization—in both cases precipitates are formed, internal volume is increased, and the matrix is depleted of chromium [3].

$Cr_2(C,N)$ precipitates were also identified at the $M_7C_3/M_{23}C_6$ transformation front. They appeared to take the place of the M_7C_3 carbides in the network, as indicated in Fig. 5, and were not seen anywhere else in the mid-wall region of the sample. It is currently unknown why $Cr_2(C,N)$ precipitates are present at such a distance from the $M_{23}C_6/ Cr_2(C,N)$ transformation front, and why they are not present anywhere else in the region between the $M_7C_3/M_{23}C_6$

Fig. 12 BSE micrograph of oxide scale at inner diameter

transformation front and the outer diameter. However, due to the similar effects on mechanical properties of nitrides and carbides [3], it is unlikely that the replacement of some carbides by carbonitrides in the inner wall has any significant effect on the tube properties.

Chromium Depletion in the Matrix and the Paramagnetic to Ferromagnetic Change

In the as-cast condition, HP alloy tubes are paramagnetic. The precipitation and growth of chromium carbides causes chromium depletion in the austenitic matrix. With increasing carburization, the matrix composition tends toward the binary Fe–Ni composition, and the matrix becomes progressively more ferromagnetic [2, 5, 7, 30–32].

The change in matrix chromium content, measured at a distance of 10 μm from the primary chromium carbide network, is shown in Fig. 14. The matrix chromium content is significantly below the typical as-cast chromium content of 25 wt%, particularly at the inner wall region. The location of the $M_7C_3/M_{23}C_6$ transformation front corresponded with a matrix chromium content of 11–12 wt%.

The change in matrix composition across the tube wall has been plotted on the ternary Fe–Cr–Ni diagram (Fig. 15) along with data representing the paramagnetic and ferromagnetic compositions (determined by the Curie temperature) [33–35]. As seen in Fig. 15, the matrix composition is in the ferromagnetic region across the entire tube wall. Although the $M_7C_3/M_{23}C_6$ transformation front, which is sometimes used as a measure of the depth of carburization [5], is only located at a distance of approximately 5 mm from the inner diameter, the large, blocky $M_{23}C_6$ carbides in the 5–7.2 mm wall region and the regions of chromium-rich η -carbide in the 3.5–7.2 mm wall region have likely

Fig. 13 BSE micrographs of the outer diameter indicating (a) the Cr-depleted zone, and (b) intragranular $Cr_2(C,N)$ and the transformation of $M_{23}C_6$ into $Cr_2(C,N)$

contributed to the chromium depletion of the matrix at the outer wall region, leading to a matrix composition that is ferromagnetic at room temperature.

NACE Etching Method

A dark etching band was clearly seen on the sample that was subjected to the NACE etching method (Fig. 16a). The etching band extended a depth of 5–5.5 mm from the inner diameter, which the standard states indicates the depth of the carburized region [11].

The location where the matrix chromium content reached 11–12 wt% corresponded with both the location of the $M_7C_3/M_{23}C_6$ transformation front (approximately 5 mm from the inner diameter) and the edge of the NACE etching band.

Fig. 14 Chromium content of the matrix across the tube wall, as determined by EDS. Results from three EDS spectra were averaged at each location

Fig. 15 Ternary Fe–Cr–Ni diagram showing the changes in matrix composition of the ex-service tube. Typical as-cast condition of HP40-Mod is denoted by a solid diamond. Matrix compositions are denoted by solid circles, and labeled with distance (mm) from the inner diameter. Asterisks denote compositions that are paramagnetic at room temperature. Open circles, squares, and triangles denote compositions that are ferromagnetic at room temperature

Two other ex-service HP alloy ethylene pyrolysis tubes (tubes B and C) were also subjected to the NACE etch for comparison with the ex-service tube for which the microstructure has been characterized (tube A).

(a)

(b)

(c)

Fig. 16 Sections of (a) tube A, (b) tube B, and (c) tube C after being subjected to the NACE etching method

The microstructure of tube B appeared very similar to tube A with regards to phases present and morphologies. However, tube B did not contain η -carbide or G-phase, and

the $M_7C_3/M_{23}C_6$ transition occurred closer to the inner diameter (4 mm). The microstructure of tube C appeared similar to that of as-cast HP alloys, however, the NbC carbides appeared to have fully transformed into G-phase.

The etching results for tubes B and C are shown in Fig. 16(b) and (c), respectively. It was seen that tube B displayed an etching band as a result of the NACE etch, however, it was not as well-defined as that of tube A, and did not extend as far into the tube wall. The etched surface of tube C appeared dull compared to the as-polished condition but was otherwise unaffected by the NACE etchant.

It should be noted that the NACE standard states that the contrast is achieved by the attack of carbides, however, the present results indicate that the contrast is due to attack of the austenitic matrix where the chromium content falls below approximately 12 wt%.

Eddy Current NDT Response

The eddy current NDT response of tubes A, B, and C, as measured by the carburization crawler under development at Quest integrity NZL Ltd, is shown in Fig. 17, where the normalized probe inductance is plotted against frequency. Tube A displays the highest normalized probe inductance across all frequencies, ranging from 1.83 at low frequencies to 1.57 at higher frequencies. A high normalized probe inductance across all frequencies indicates that the entire tube wall is highly carburized, which is consistent with the matrix of tube A being ferromagnetic across the entire tube wall as indicated by the matrix composition profile. The slight drop in normalized probe inductance at high frequencies indicates the outer wall region is carburized to a slightly lesser extent than the inner wall, which is consistent with microstructural observations and the NACE etch results.

Tube B displays the same trend in normalized probe inductance as tube A, albeit at a slightly lower range, indicating that tube B is less carburized than tube A, which is consistent with the $M_7C_3/M_{23}C_6$ transition occurring closer to the inner diameter in tube B, and the lack of η -carbide to contribute to the chromium depletion. The normalized probe inductance for tube B ranges from 1.72 at low frequencies to 1.50 at high frequencies. The eddy current response of tube B indicates carburization to a lesser extent than tube A, and correlates well to the NACE etch results.

Tube C exhibits a constant normalized probe inductance of 1.02 across all frequencies. An un-carburized tube would be expected to have a normalized probe inductance below that of the probe in air, i.e., <1. The response of tube C indicates that there is little or no carburization. Tube C did not respond to the NACE etchant, and did not display a chromium carbide transition in the microstructure, which is consistent with little or no carburization, however, slight carbide coarsening may have caused chromium depletion

Fig. 17 Eddy current NDT response (normalized probe inductance vs. frequency) of tubes A, B, and C

in the matrix, leading to a normalized inductance value slightly greater than 1.

Conclusions

- Three important phase transformations were identified in the ex-service HP alloy tube:
 - $M_{23}C_6$ transformed to M_7C_3 , with the transformation front located a distance of approximately 5 mm from the inner diameter.
 - $M_{23}C_6$ transformed to $Cr_2(C,N)$ at the outer diameter of the tube, as a result of exposure of the tube's outer surface to flue gases during service. $Cr_2(C,N)$ carbonitrides were also observed at the $M_7C_3/M_{23}C_6$ transformation front, appearing to take the place of M_7C_3 carbides, but their presence at the transformation front is currently unexplained.
 - NbC transformed to η -carbide in the 3.5–7.2 mm region of the wall. η -carbide was identified rather than G-phase due to significant differences in the chromium and nickel content between the two phases. As η -carbide contains a significant amount of chromium, it is likely that the NbC-to- η -carbide transformation contributes to the chromium depletion of the matrix. Although there is information in literature regarding the temperature ranges over which the NbC-to-G-phase and NbC-to- η -carbide transformations occur in HP-Nb alloys, the conditions under which these data were collected differ significantly from the carburizing conditions experienced by pyrolysis tubes in service, so are not directly comparable.

- The M_7C_3 carbides appeared to contain a separate phase, identified as austenite. EBSD analysis on contained austenite–matrix pairs determined that 69% of the pairs obtained an orientation typical of a cube–cube orientation, and 18% obtained an orientation typical of a twin orientation. Deep etching in glyceric acid showed the M_7C_3 carbides appeared to be composed of many rounded grains, and that regions of austenite that appeared as open matrix in the as-polished condition would have appeared enclosed by the M_7C_3 carbides had the plane of polish been deeper into the sample. It seems likely that the austenite regions that appear contained by the M_7C_3 carbides are actually connected to the matrix in three dimensions, and may appear contained as a result of sectioning effects.
- The edge of the NACE etching band corresponds to the $M_{23}C_6/M_7C_3$ transformation front, which corresponded with a matrix chromium content of approximately 12 wt%. Rather than attack of carbides, it appears that the NACE etch contrast occurs due to attack of the austenitic matrix where the chromium content falls below approximately 12 wt%.
- Severe chromium depletion of the matrix was seen across the tube wall, but particularly near the inner diameter region where the matrix chromium content dropped as low as 4 wt%. A comparison with Curie Temperature data indicated that the matrix is ferromagnetic across the entire tube wall.
- The present results indicate that the eddy current method is able to detect and measure carburization non-destructively.

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